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ELECTRICAL CONDUCTIVITY IN THE FUSED SALT SYSTEM $PbCl_2$ - LiCl - KCl

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by

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ABSTRACT

Electrical conductivities have been determined in the ternary fused salt system $PbCl_2$ - LiCl - KCl at temperatures between 334 and 542°C using an ac bridge with a silica glass capillary cell. Specific conductivity increased linearly with temperature (T). Within the range of compositions studied, generally from 0.1 to 0.5 $PbCl_2$ mole fraction (1-y) and from 0.3 to 0.7 LiCl/(KCl+LiCl) mole ratio (t), specific conductivity increased with increasing LiCl content and decreased with increasing KCl content in the melt. Molar and equivalent conductivities were non-linear functions of $PbCl_2$ mole fraction along lines of constant t. A 12-term polynomial expression in y, t and T, fitted to the specific conductivity data, adequately described the experimental results.

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CONDUCTIVITÉ ÉLECTRIQUE DANS LE SYSTÈME DES SELS FONDUS $PbCl_2$ - LiCl - KCl

par

S.A. Mikhail*, C.R.K. MacLean** et A.H. Webster*

SOMMAIRE

On a déterminé des conductivités électriques dans le système ternaire des sels fondus $PbCl_2$ - LiCl - KCl à des températures entre 334 et 542°C en employant un pont à courant alternatif avec une cellule capillaire en verre de silice. La conductivité spécifique accroissait linéairement avec la température (T). Dans la rangée des compositions étudiées, généralement de 0.1 à 0.5 pour la fraction molaire de $PbCl_2$, (1-y), et de 0.3 à 0.7 pour le rapport molaire LiCl/(KCl + LiCl), (t), la conductivité accroissait avec une augmentation de contenu en LiCl et décroissait avec une augmentation de contenu en KCl dans la fonte. Les conductivités molaires et équivalentes étaient des fonctions non-linéaires de la fraction molaire de $PbCl_2$ le long des lignes de t constant. Une fonction polynôme à 12 termes en y, t et T, ajustée aux données de conductivité spécifique, a décrit assez bien les résultats expérimentaux.

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INTRODUCTION

In response to recent trends towards more environmental protection, and more stringent in-plant hygiene levels, strong efforts are being made to seek alternative methods for the production of lead metal. The conventional pyrometallurgical methods of lead production are facing stricter regulations to keep the lead and sulphur oxide emissions to the lowest possible levels.

The extraction of lead from lead concentrates by hydrometallurgical methods is currently under investigation at the Canada Centre for Mineral and Energy Technology (CANMET). In this project, lead concentrates are leached with hot ferric chloride and brine solution to produce pure lead chloride for electrolysis either as an aqueous solution or as a molten salt to obtain the metal. A similar process has been reported in a series of publications by a group at the U.S. Bureau of Mines (1-3). In their work, the concentrate was leached in a solution of ferric and sodium chlorides at 100°C according to the reaction:

$$PbS + 2FeCl_3 \xrightarrow{NaCl} PbCl_2 + 2FeCl_2 + S^\circ$$

Pure lead chloride was crystallized from the solution and was electrolysed in a molten-salt bath of LiCl-KCl eutectic composition (58.8 mol % LiCl and 41.2 mol % KCl). The choice of an optimum temperature and composition for the electrolyte was made after investigating operational parameters such as current density, current and energy efficiencies, and lead chloride fuming. The authors reported that the best overall results for the electrolysis were obtained with 40-70 mass % $PbCl_2$ in the eutectic at 450°C (2). Some fuming occurred when the temperature of the molten bath exceeded 450°C.

Due to its desirable characteristics such as a low melting point (348°C), good thermal stability and high electrical conductance, the LiCl-KCl eutectic melt has been widely used as a solvent in numerous electrochemical studies (4). Its selection for $PbCl_2$ electrolysis was based on various considerations. For instance, lead chloride, on its own, was found to be unsuitable for electrolysis due to the high vapour pressure at temperatures above the melting point and some solubility of lead metal in the chloride.

The addition of alkali chlorides such as LiCl, KCl and NaCl to lead chloride reduced the melting point of the bath and decreased volatilization substantially (2). The addition of LiCl improved the conductivity, but KCl, which has a larger cation, reduced $PbCl_2$ volatilization more effectively than LiCl. The best overall result, as mentioned previously, was attained by using a LiCl-KCl eutectic as a solvent for $PbCl_2$ (2). A critical analysis of published data on melt preparation, liquidus temperatures, specific conductivity, density, viscosity and surface tension in the LiCl-KCl system was reported by Janz et al. (5,6).

The properties of the ternary system $PbCl_2$ - LiCl - KCl that are important for its use as a molten salt electrolyte for the production of lead have been studied by only a few investigators. The phase diagram was determined by Bergman et al. using a visual polythermal method (7). They reported the formation of an incongruently melting ternary compound but the exact composition was not determined. Densities and molar volumes of various compositions in the temperature range 440-780°C were reported by Gutiérrez and Toguri (8). Calculated activities and vapour pressures at different temperatures and a calculated phase diagram were reported by Skeaff et al. (9). Thermodynamic properties of the melt were determined by Lantratov (10) and by Takahashi (11) on the basis of emf measurements over a range of temperatures.

The aim of the present work is to determine the electrical conductivity of various compositions in the ternary system $PbCl_2$ - LiCl - KCl on which there is an apparent defficiency in the literature. This parameter is of major importance in the selection of a suitable composition for the electrolyte in the electrowinning of lead.

Conductivity measurements in the boundary systems LiCl-KCl and $PbCl_2$-KCl were done by a few investigators and a critical survey of the available literature was reported by Janz et al. (5,6). There is no available data, however, on the electrical conductance of the third boundary system $PbCl_2$-LiCl.

MATERIALS AND EXPERIMENTAL PROCEDURE

The starting materials were "Baker Analysed" reagent grade $PbCl_2$ powder (99.9%), "Baker Analysed" reagent grade KCl crystals and specially prepared anhydrous LiCl (-60 mesh, 99.8%) from Cerac Inc., U.S.A. Semi-quantitative spectrographic analysis indicated the following major impurities in the $PbCl_2$: Al (0.01%), Fe (0.001%), Si (0.001%), Cu (0.007%), Ag (0.0009%) and Mg (0.0003%); in the KCl: Fe (0.001%), Ca (0.001%) and Cu (0.005%); and in the LiCl: K (0.01-0.1%), Si (0.005%), Na (0.005%), Cu (0.001%), Al (0.001%) and Mg (0.001%). All materials were predried at 150°C under vacuum for several hours and stored in a dry box. The starting LiCl-KCl mixtures were further subjected to an extensive HCl-Ar treatment according to the method of Laitinen et al. (12) to remove the last traces of moisture and to prevent hydrolysis. The molten salt solution was then filtered through a glass frit into a silica glass receiver and kept under vacuum to remove trapped gases before cooling. The apparatus used in the HCl treatment and filtration is shown in Figure 1. The results of pH measurements of some aqueous solutions of representative samples after the treatment did not indicate any signs of hydrolysis. Moreover, etching of the glass apparatus was minimal when the samples were treated with HCl. Some tests, carried out without the treatment, resulted in noticeable etching.

The required amount of $PbCl_2$ was added to the cooled LiCl-KCl mixture to make the desired ternary composition and the receiver was placed in the conductivity cell assembly, inside the dry box, ready for measurements.

Among the different cell designs for conductivity measurements, the capillary cell is the most suitable and most commonly used in molten salt studies. Due to the high specific conductivity, accurate measurements require the use of a cell with a large cell constant (>200 cm^{-1}), i.e., with a long narrow conductance path. The capillary cell fulfills this requirement. Figure 2 shows the twin capillary cell used in the present study. The upper part of the cell was made of Pyrex glass with 4 inlets on top to accommodate two electrode tubes, a gas inlet tube and a thermocouple tube, and one side tube for the gas outlet or vacuum. The electrode tubes were made of 6 mm i.d. silica tubing with silica capillaries about 30 mm long and 1 mm i.d. attached to the ends. The cell design allowed the raising and lowering of any of the tubes through seals made of Tygon tubing

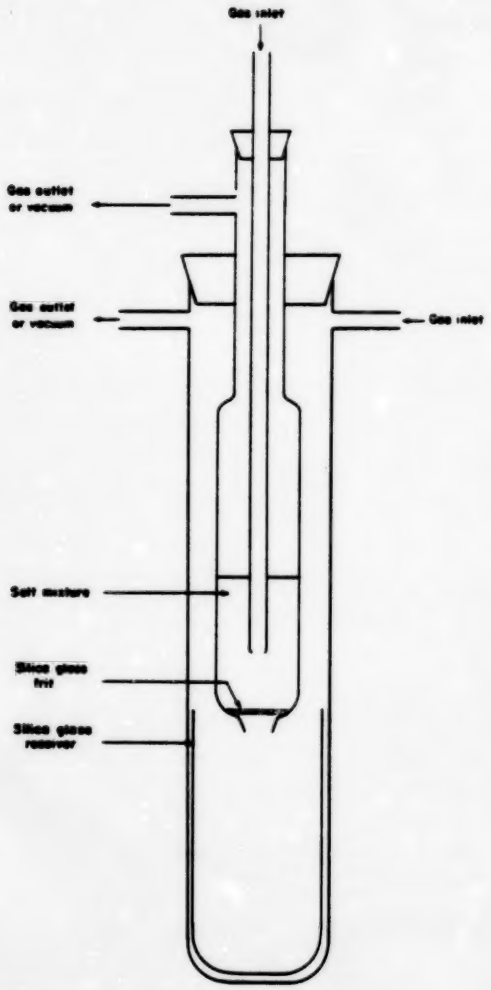

Figure 1: Assembly for HCl treatment and filtration of starting materials.

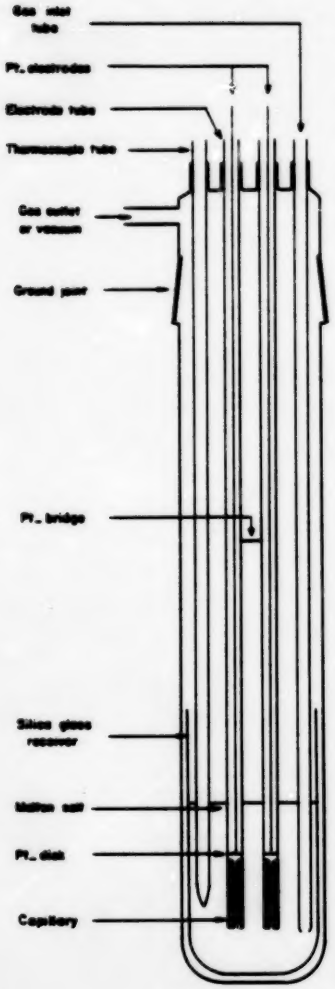

Figure 2: Conductivity cell

and ring clamps. The spacing between the electrode tubes was maintained by a bridge made of thick platinum wire covered with Teflon tape. The lower part of the cell, which accommodated the receiver with the charge, was made of silica tubing with an internal diameter of 40 mm.

The electrodes were platinum disks of 0.16 mm thickness and about 4 mm diameter welded to platinum wires of 0.4 mm diameter. In the preliminary experiments, the electrodes were carefully platinized using platinic chloride solution. It was found later, however, that platinizing did not have any detectable effect on the readings. A Beckman conductivity bridge, Model RC-18A, with 1 and 3 kHz frequences was used in this work. All measurements were conducted using both frequencies and the differences were only about 0.1%; this agrees well with recent reports by Carmichael and Flengas (13) and Benhenda and Lesourd (14).

The specific conductivity κ may be found using:

$$\kappa = \frac{K_{cell}}{R} = k.\ K_{cell} \qquad (1)$$

where R is the measured resistance, k is the measured electrical conductance and K_{cell} is the cell constant. In the present study, the cell constant was determined by measuring the electrical conductance of a known KCl solution at 25°C (15). A water bath was used to maintain the temperature of the cell constant at 25°C. The cell constant was in the order of 700 cm^{-1}. The specific conductivity of the molten salt was then determined by measuring the electrical conductance of the melt and substituting this value together with the cell constant in equation 1.

RESULTS AND DISCUSSION

Electrical conductivities of 28 compositions in the ternary system $PbCl_2$ - LiCl - KCl were measured at different temperatures between 334 and 542°C. For each composition, the lower limit of the temperature range at which the measurements were taken was determined by the ternary liquidus temperature. Volatilization of lead chloride determined the upper temperature limit.

For the identification of the ternary compositions, two compositional parameters, y and t, were defined as follows:

$$y = 1 - X_{PbCl_2}$$

$$= X_{LiCl} + X_{KCl},$$

$$\text{and} \quad t = \frac{X_{LiCl}}{X_{LiCl}+X_{KCl}}$$

where X is the mole fraction of the assigned component. Therefore, in the ternary system, a y value of 1 represents the boundary system LiCl-KCl, a t value of 0 represents the system $PbCl_2$-KCl and a t value of 1 represents the system $PbCl_2$-LiCl. Twenty-four selected compositions could then be identified by t values of 0.3, 0.4, 0.5, 0.588 and 0.7 and y values of 0.5, 0.6, 0.7, 0.8, and 0.9 for each value of t (omitting t=0.3 with y=0.9). The four remaining compositions could be identified by the t value of 0.588 and y values of 0.2, 0.3, 0.4 and 1.0.

A summary of the experimental results is presented in Table 1 as a least squares fit of the electrical conductivity versus temperature data according to the following equation:

$$\kappa = a + bT \qquad (2)$$

where κ is the specific conductivity in siemens cm^{-1} (ohm^{-1} cm^{-1}), T is the temperature in K, and a and b are constants. As can be seen from Table 1, deviations from equation 2 are small.

Conductivity measurements at various temperatures were made on heating and on cooling and several experiments were conducted more than once. The reproducibility of the results was found to be very high. The cell constant was measured before and after each series and the difference was less than 0.4%. The Pt-Pt/13% Rh measuring thermocouple was checked against a certified standard thermocouple and the maximum difference was found to be less than 0.3°C at 500°C. Volatilization of $PbCl_2$ was noticeable at temperatures above 450°C and for ternary compositions with

Table 1.: Least squares fit of the electrical conductivity (κ, $S.cm^{-1}$) vs. temperature (T,K) for various values of the composition parameters t and y for the system $PbCl_2$-LiCl-KCl.

$PbCl_2$ Mole fraction (1-y)	Temp. Range, °C	$\kappa = a + bT$		Standard Error of Estimate	Correlation Coefficient
		-a	$bx10^3$		
t = 0.30					
0.20	479-542	1.9680	4.071	±0.0025	0.9997
0.30	400-527	1.9413	4.089	0.0025	0.9999
0.40	378-525	1.9365	4.128	0.0053	0.9997
0.50	405-524	1.8794	4.110	0.0045	0.9997
t = 0.40					
0.10	465-538	2.2129	4.592	0.0027	0.9998
0.20	387-514	2.2120	4.597	0.0030	0.9999
0.30	352-515	2.1457	4.529	0.0080	0.9995
0.40	365-515	2.0341	4.410	0.0062	0.9997
0.50	390-516	2.0172	4.426	0.0049	0.9997
t = 0.50					
0.10	395-526	2.4035	5.104	0.0072	0.9995
0.20	334-518	2.3124	4.946	0.0086	0.9996
0.30	340-511	2.2061	4.809	0.0110	0.9992
0.40	363-515	2.0677	4.625	0.0063	0.9997
0.50	393-515	2.0912	4.647	0.0053	0.9997
t = 0.588					
0.00	379-511	2.8801	6.099	0.0074	0.9996
0.10	383-515	2.4681	5.462	0.0089	0.9994
0.20	388-497	2.2738	5.162	0.0057	0.9996
0.30	396-497	2.1338	4.920	0.0062	0.9995
0.40	383-499	2.1947	4.960	0.0093	0.9991
0.50	378-517	2.1902	4.924	0.0072	0.9996
0.60	377-512	2.3500	5.094	0.0061	0.9997
0.70	439-502	2.2861	4.972	0.0017	0.9999
0.80	455-505	2.3173	4.970	0.0020	0.9998
t = 0.70					
0.10	454-524	2.1585	5.558	0.0106	0.9976
0.20	455-526	2.1973	5.445	0.0052	0.9993
0.30	437-526	2.0754	5.144	0.0047	0.9996
0.40	424-528	2.1235	5.105	0.0068	0.9993
0.50	402-524	2.2498	5.159	0.0072	0.9995

high LiCl contents. The accumulated experimental uncertainty in the cell constant, temperature and salt composition may be estimated as ±2%.

Conductivity data for the LiCl-KCl eutectic (58.8 mol % LiCl - 41.2 mol % KCl) in the present work were found to be 1.8% lower than those published by Van Artsdalen and Yaffe (16) for the same composition over the temperature range 380-520°C. This may be attributed to the different methods used in preparing the starting materials to avoid hydrolysis.

The data obtained from all tested compositions indicated that the conductivity of the ternary molten salt solutions increased steadily with temperature and with LiCl content. Figure 3 shows typical results of two series of experiments for ternary compositions with low (t=0.3) and high (t=0.7) LiCl contents and different mole fractions of $PbCl_2$.

The influence of LiCl on the conductivity of the molten salt solutions is consistent with the conductivity of fused LiCl, which is the highest of the three salts in the system. The specific conductivity of $PbCl_2$ is intermediate between those of LiCl and KCl and so, in general, it would be expected that increasing the mole fraction of $PbCl_2$ would lower the conductivity in the high LiCl region (e.g., t=0.7) and raise the conductivity in the high KCl region (e.g., t=0.3). In the binary system $PbCl_2$-KCl, Lantratov and Moiseeva (17) reported minima in the specific conductivity isotherms at compositions in the range 0.3 to 0.34 mole fraction $PbCl_2$. From Fig. 3 it appears that this minimum in specific conductivity does not extend to compositions with t=0.3.

From Equation 2 the conductivity of each ternary composition was determined at eight selected temperatures, namely 350, 375, 400, 425, 450, 475, 500 and 525°C by substituting the relevant constants from Table 1. The relationship between κ and t, for each $PbCl_2$ mole fraction, was then plotted at each of the selected temperatures and the isoconductivity compositions were determined graphically. Isoconductivity lines within the ternary liquidus regions are shown in Figures 4-11. From the direction of the lines it is apparent that the effect of $PbCl_2$ content on the conductivity of the melt is small in comparison to the effect of the LiCl/KCl ratio.

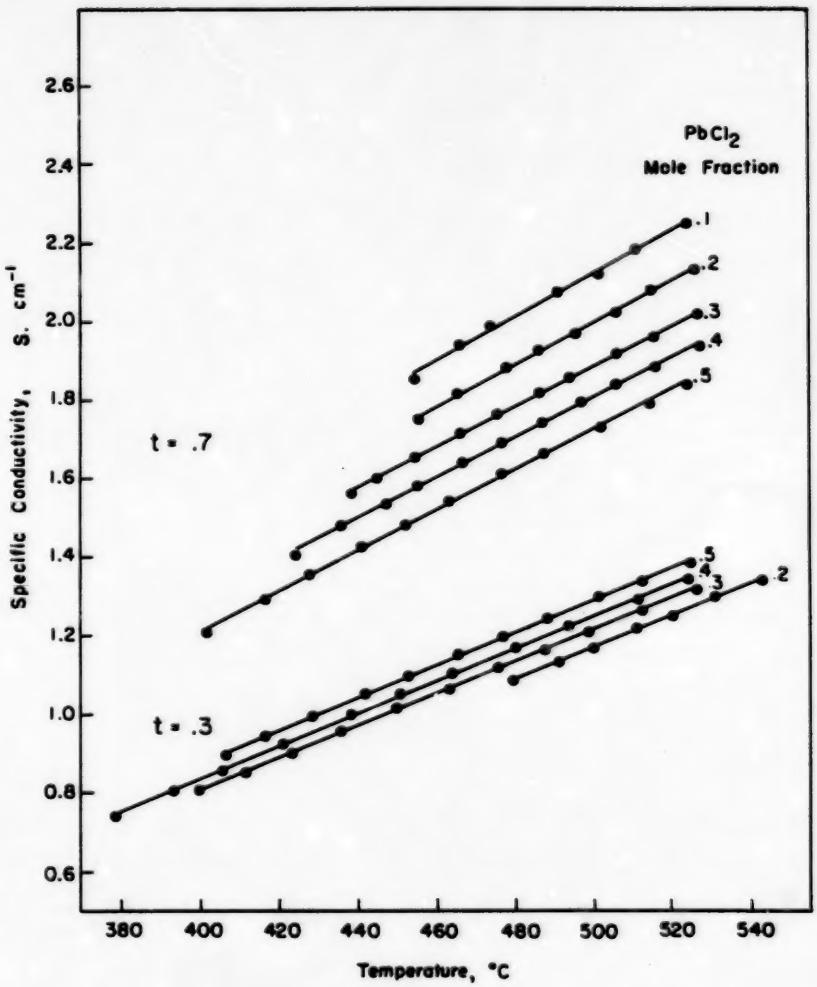

Figure 3: Temperature dependence of conductivity in the system $PbCl_2$-LiCl-KCl.

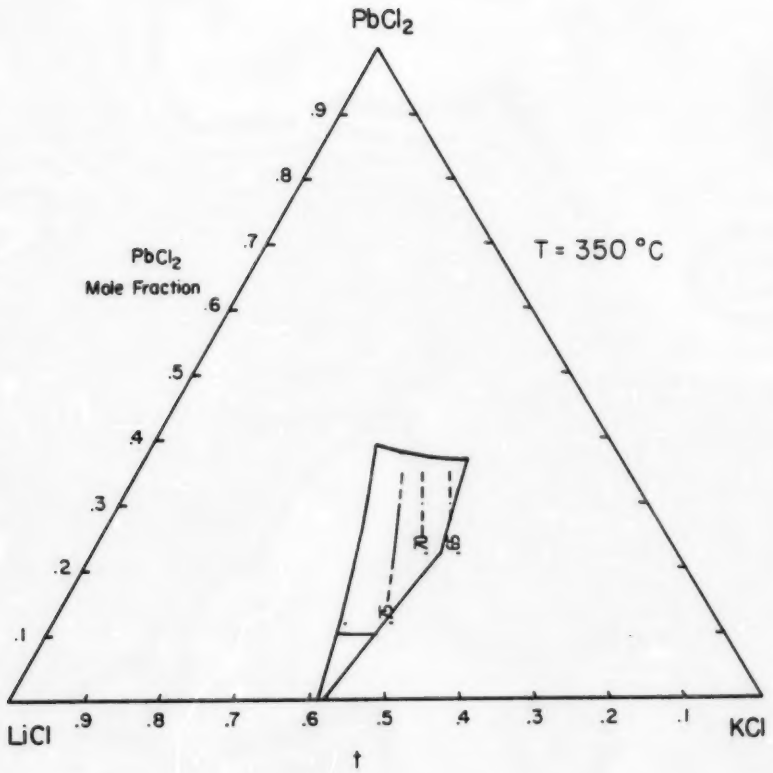

Figure 4: Isoconductivity lines in the system $PbCl_2$-LiCl-KCl at 350°C

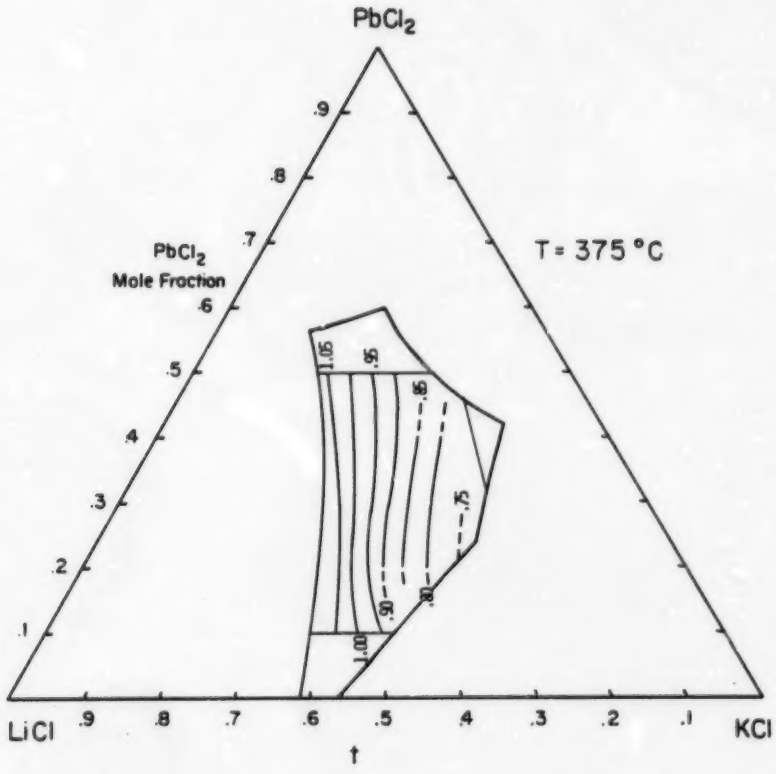

Figure 5: Isoconductivity lines in the system $PbCl_2$-LiCl-KCl at 375°C

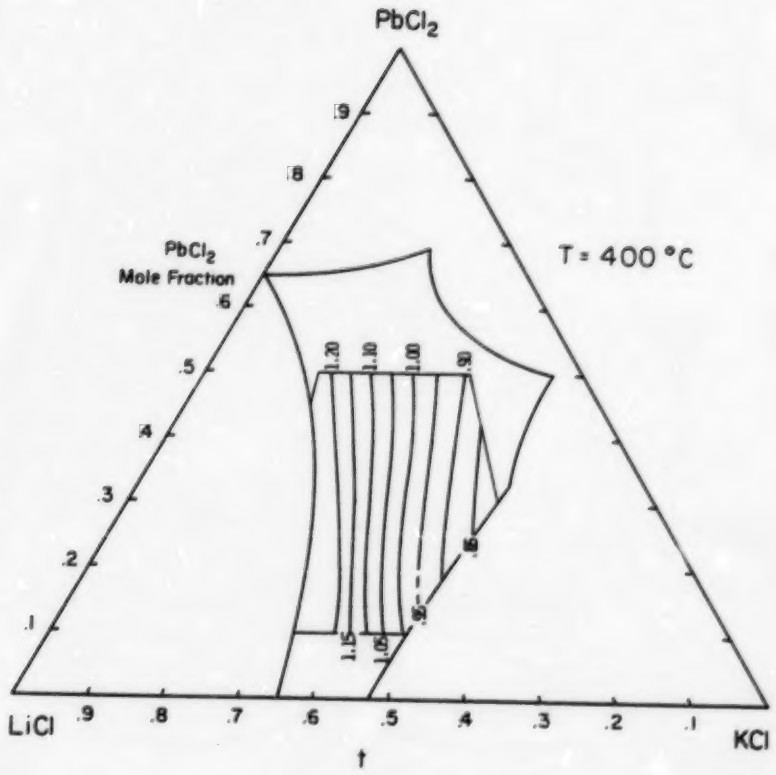

Figure 6: Isoconductivity lines in the system $PbCl_2$-LiCl-KCl at 400°C

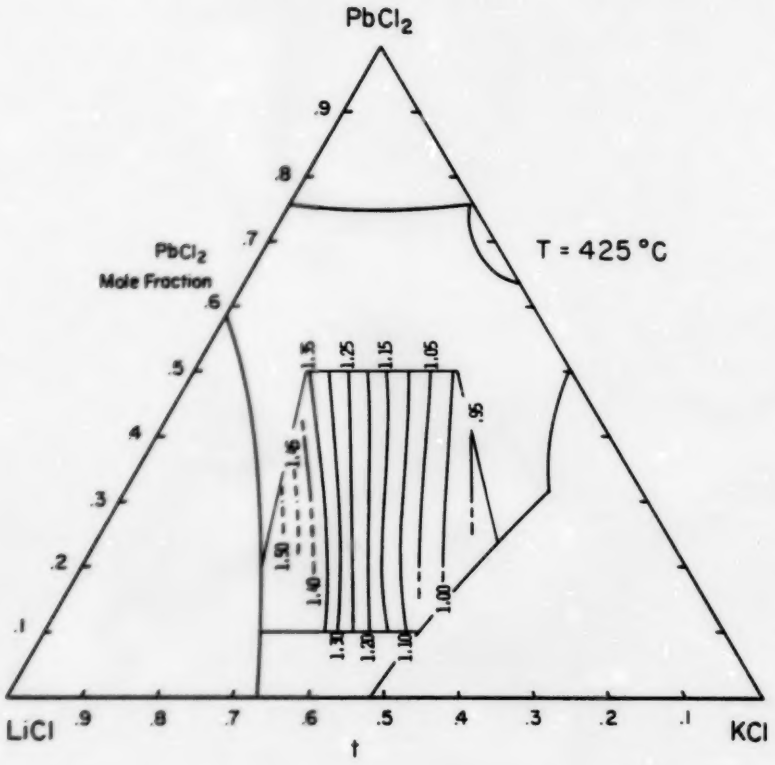

Figure 7: Isoconductivity lines in the system $PbCl_2$-LiCl-KCl at 425°C

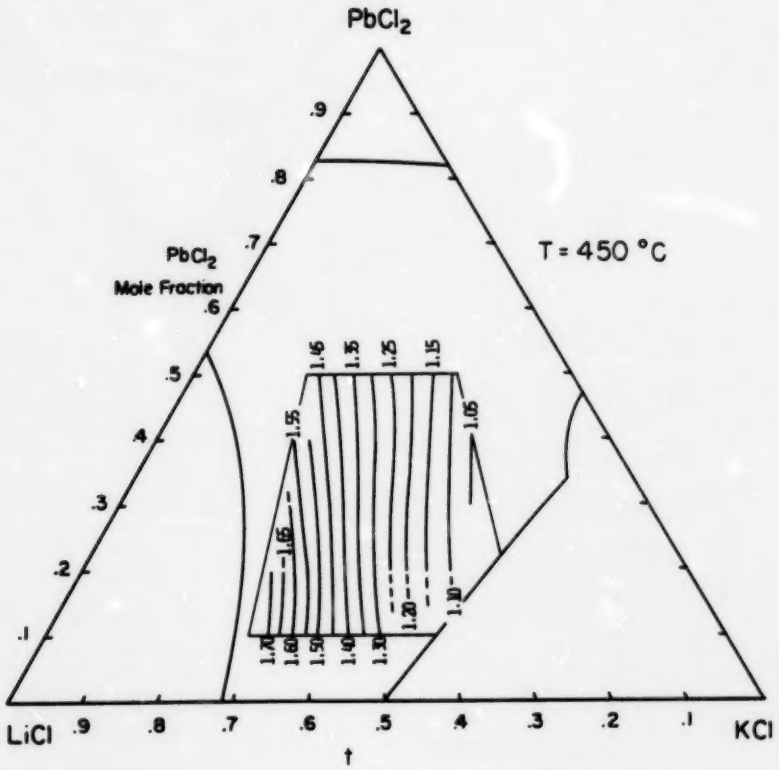

Figure 8: Isoconductivity lines in the system $PbCl_2$-LiCl-KCl at 450°C

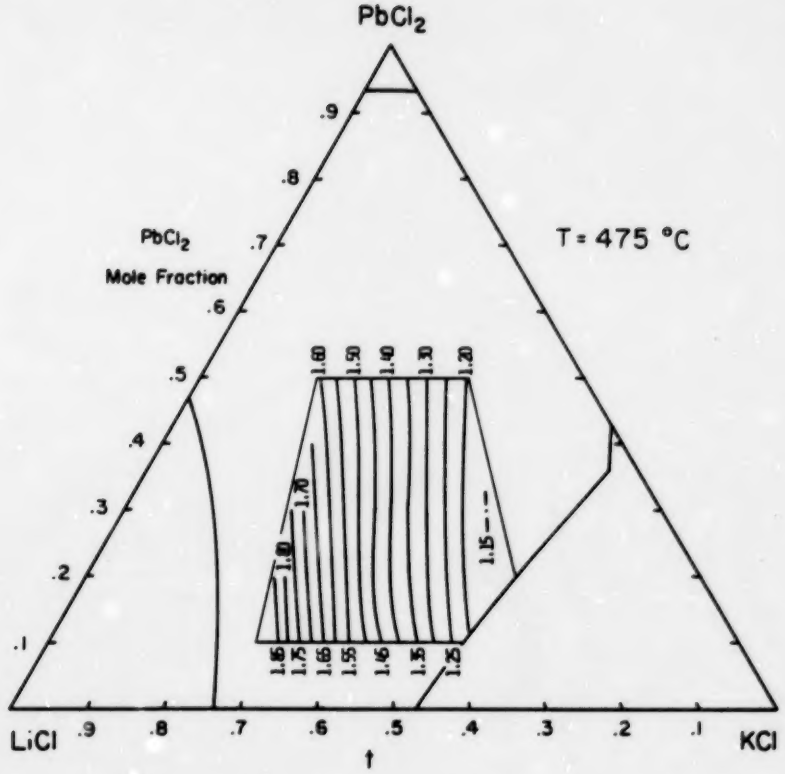

Figure 9: Isoconductivity lines in the system $PbCl_2$-LiCl-KCl at 475°C

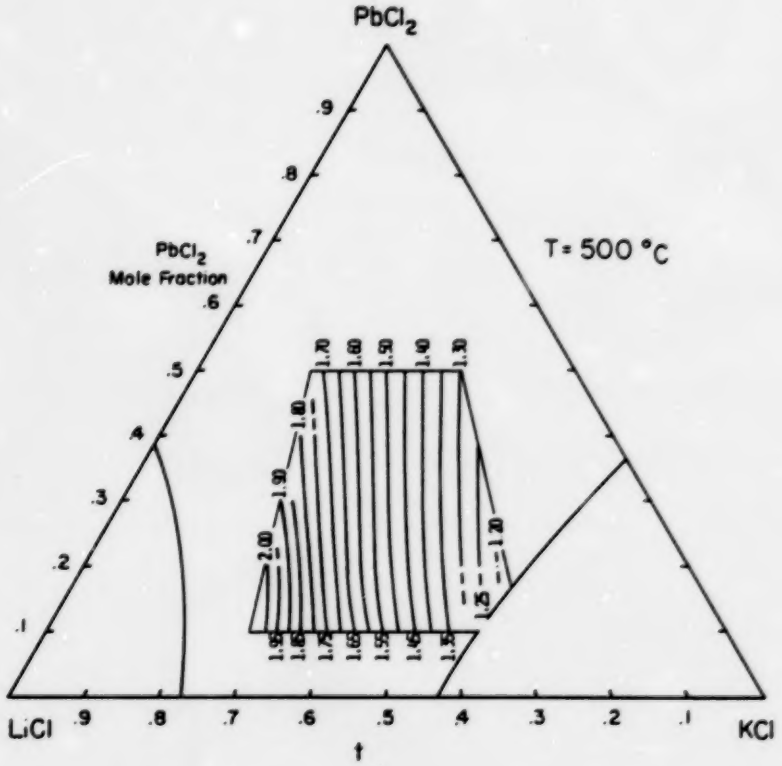

Figure 10: Isoconductivity lines in the system $PbCl_2$-LiCl-KCl at 500°C

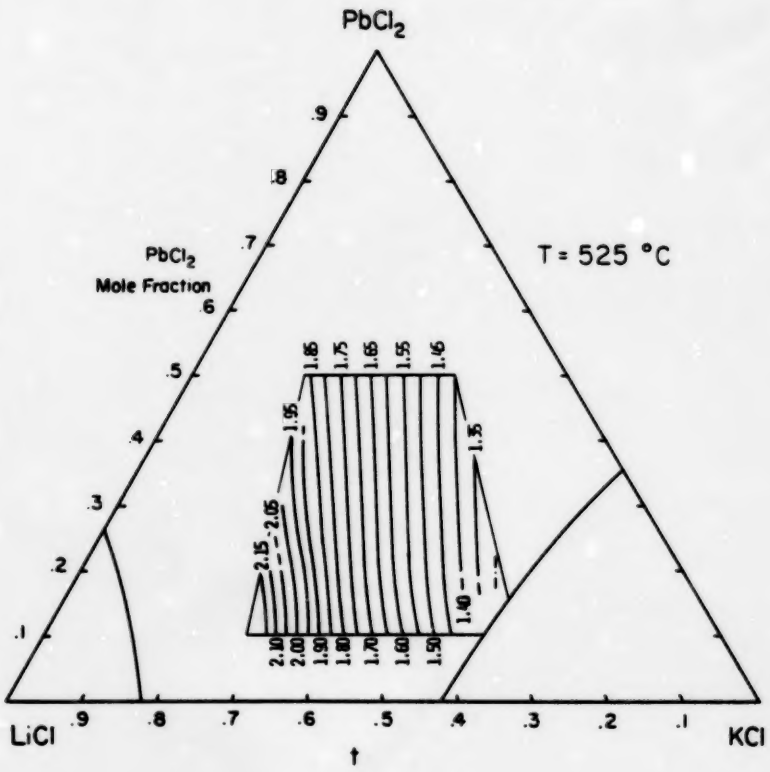

Figure 11: Isoconductivity lines in the system $PbCl_2$-LiCl-KCl at 525°C

The experimental data for the conductivities at different temperatures and compositions (279 data points) were found to fit an equation of the following type:

$$\kappa = [a_0 + a_1y + a_2y^2 + a_3yt + a_4yt^2 + a_5ty^2] + T[b_0 + b_1y + b_2y^2 + b_3yt + b_4yt^2 + b_5ty^2] \quad (3)$$

where $a_0 = -3.192925$ $\quad b_0 = 6.11579 \times 10^{-3}$

$a_1 = 5.52791$ $\quad b_1 = -7.79503 \times 10^{-3}$

$a_2 = -4.61250$ $\quad b_2 = 5.44181 \times 10^{-3}$

$a_3 = -3.55432$ $\quad b_3 = 4.08188 \times 10^{-3}$

$a_4 = 1.60872$ $\quad b_4 = 0.440861 \times 10^{-3}$

$a_5 = 1.51924$ $\quad b_5 = -0.260476 \times 10^{-3}$

Standard error of estimate = $\pm$ 0.0129 S. cm^{-1}

Only eight experimental points deviated from the predicted values of the equation by more than 2% (<2.9%). The deviation may be explained on the basis of experimental difficulties at those specific compositions. Equation 3 may therefore be used to estimate, approximately, the specific conductivity of any ternary composition at any temperature within the experimental region used in the present investigation.

To determine the molar conductivity, Λ_M, the following expression was used:

$$\Lambda_M = \kappa . V_M \quad (4)$$

where κ is the specific conductivity and V_M is the molar volume. The molar volume was determined by using the density data reported by Gutiérrez and Toguri (8) for various compositions in the ternary system $PbCl_2$-LiCl-KCl in the expression:

$$V_m = \frac{\sum X_i M_i}{\rho} \quad (5)$$

where X_i and M_i are the mole fraction and the molecular weight of component i in the solution, and ρ is the density of the solution. The calculated molar volumes (cm^3) for 10 ternary compositions at different temperatures (50 data points) (8) were found to fit an equation similar to equation 3:

$$V_M = [c_0 + c_1y + c_2y^2 + c_3yt + c_4yt^2 + c_5ty^2] + T[d_0 + d_1y + d_2y^2 + d_3yt + d_4yt^2 + d_5ty^2] \quad (6)$$

where $c_0 = 41.417953$ $\quad d_0 = 1.98313 \times 10^{-2}$

$c_1 = -24.2869$ $\quad d_1 = 1.74725 \times 10^{-2}$

$c_2 = 24.8809$ $\quad d_2 = -3.58357 \times 10^{-2}$

$c_3 = 26.2377$ $\quad d_3 = -5.87922 \times 10^{-2}$

$c_4 = -5.97338$ $\quad d_4 = 0.735897 \times 10^{-2}$

$c_5 = -56.1904$ $\quad d_5 = 7.83140 \times 10^{-2}$

Standard error of estimate = ± 0.24 cm^3

The maximum deviation from the values predicted by Equation 6 was 1% and hence the molar volume of any ternary mixture could be calculated at any temperature, within the experimental region, with fair accuracy.

As an example, the molar conductivities were calculated, using Equations 2, 4 and 6, and correlated to $PbCl_2$ mole fraction at 450°C for different values of t as shown in Figure 12. Equation 2 was chosen for the calculation of the specific conductivity since, unlike Equation 3, it does not assume any particular relationship between conductivity and composition.

The equivalent conductivity is given by:

$$\Lambda_E = \kappa . V_E = \kappa \frac{\sum f_i E_i}{\rho} \quad (7)$$

where V_E is the equivalent volume, f_i is the equivalent fraction, and $E_i = M_i/z_i$ is the equivalent weight of component i; z_i is the number of moles of charge per mole of salt, i.e., 2 for $PbCl_2$ and 1 for KCl and LiCl. It can be shown that

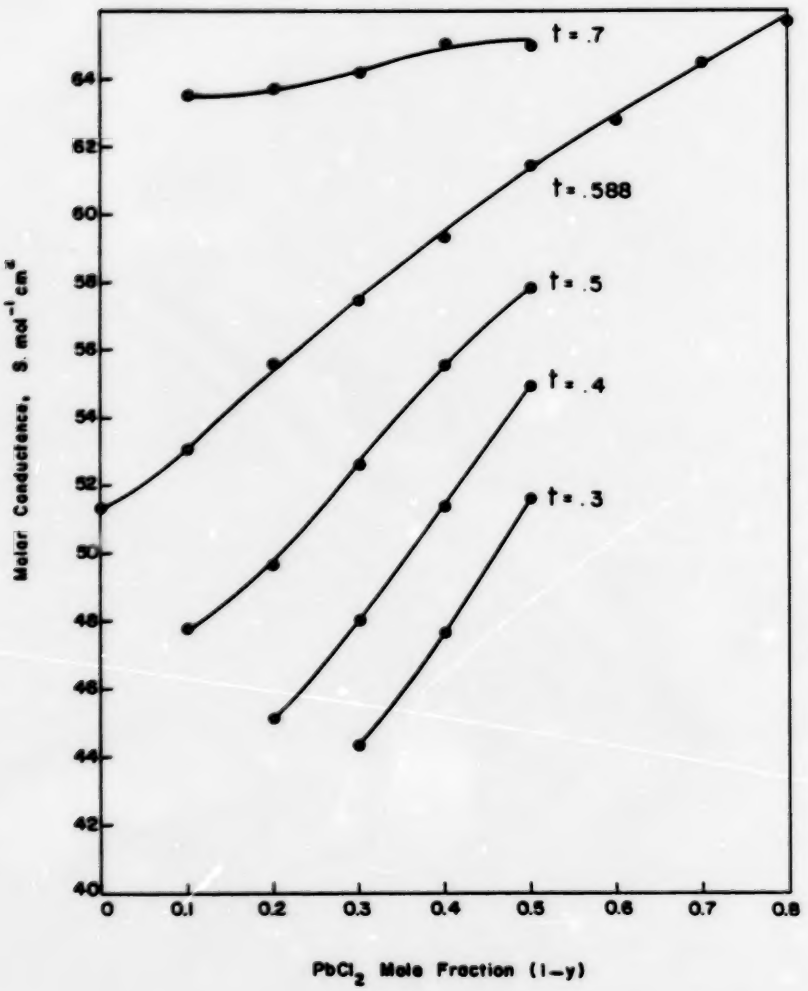

Figure 12: The dependence of the molar conductivities in the ternary system $PbCl_2$-LiCl-KCl on $PbCl_2$ mole fraction at 450°C

$$\sum f_i E_i = \frac{\sum X_i M_i}{\sum X_i z_i} \qquad (8)$$

and hence the equivalent conductivity can be calculated from

$$\Lambda_E = \kappa \frac{V_M}{\sum X_i z_i} = \frac{\Lambda_M}{\sum X_i z_i} \qquad (9)$$

Equivalent conductivities at 500°C are shown as functions of $PbCl_2$ mole fraction in Figure 13. Using equivalent conductivity, comparisons can be made on the basis of equal quantities of ionic charge, assuming the salts to be fully ionized. Differences in equivalent conductivity can therefore be interpreted in terms of ionic mobilities and of ion-ion interactions, which in extreme cases may involve complex ion formation. The increase in equivalent conductivity with increasing t reflects the higher mobility of the Li^+ ion, associated with its smaller ionic radius (0.068 nm) as compared to the K^+ ion (0.133 nm).

The plot for t=0.3 in Figure 13 shows hardly any indication of a minimum in equivalent conductivity. Equivalent conductivity determinations in the KCl-$PbCl_2$ system (t=0) reported by Lantratov and Moiseeva (17) and by Bloom and Heymann (18) show definite minima at about 0.4 mole fraction $PbCl_2$; these minima have been attributed to the formation of complex ions, possibly $PbCl_4^{2-}$, in the melt (19). The presence of such complex ions in this system is consistent with the formation of the solid compound K_2PbCl_4 (7). Raman spectra of fused $PbCl_2$-KCl have been interpreted in terms of complex $PbCl_3^-$ ions (20). Investigtions of vapour pressures in the system $PbCl_2$-KCl (21,22) have shown marked deviations from ideal behaviour, which have been interpreted in general terms by complex formation. Determinations of excess partial molar free energies, derived from emf measurements in the $PbCl_2$-KCl system, have been explained on the basis of complex ion formation (23). Similar measurements in the $PbCl_2$-KCl-LiCl system have indicated that the effects on excess free energy extend into the ternary system (10). It appears, however, that only a vestige of the effect of complex ion formation on equivalent conductivity extends into the ternary system to compositions corresponding to t=0.3.

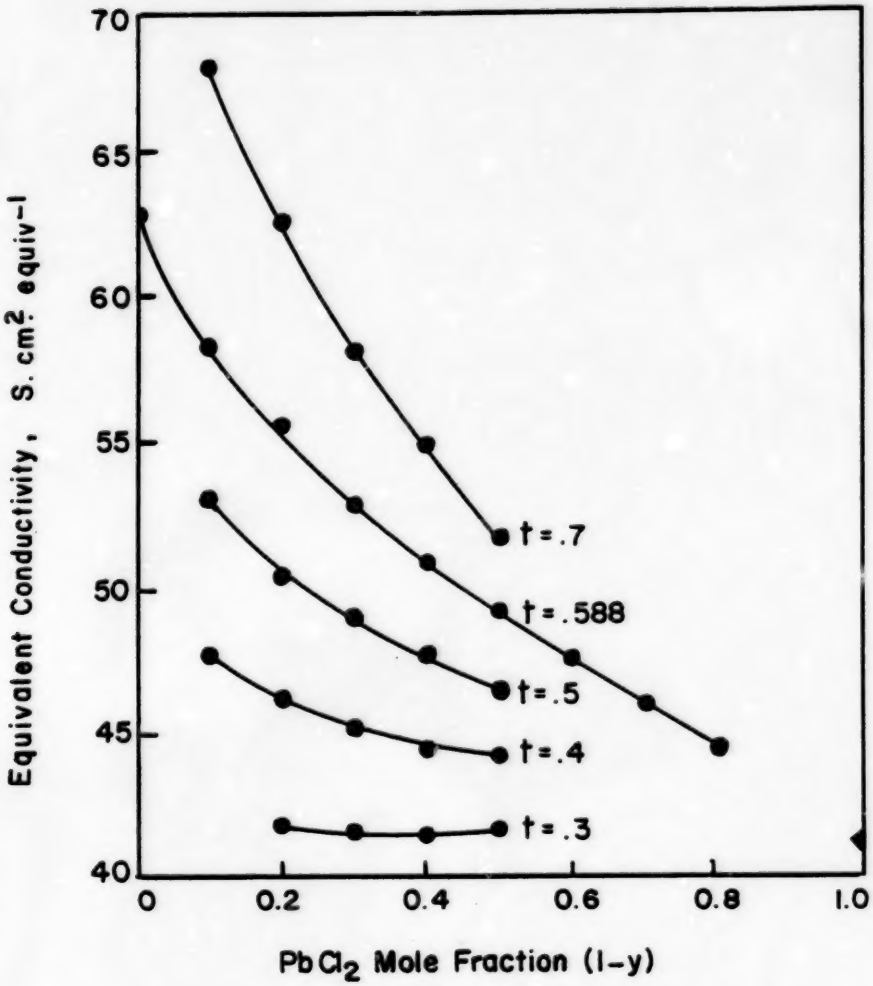

Figure 13: Equivalent conductivity in the system $PbCl_2$-LiCl-KCl at 500°C. $PbCl_2$ equivalent conductivity from Lantratov and Moiseeva (17)

Formation of complex ions appears to be favoured in alkali chloride - lead chloride systems with increasing cation size from K^+ to Rb^+ to Cs^+ (19). The smaller more polarizing cations, Na^+ and Li^+, seem to preclude association between Pb^{2+} and Cl^-. In the ternary system $PbCl_2$-KCl-LiCl, as the mean radius of the alkali cations decreases with increasing t, the tendency for complex ion formation becomes less and the effect on equivalent conductivity diminishes to the point when the conductivity minimum is no longer observed.

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